Multi-electron atoms (II)
Hartree Approximation

<u>For an atom with Z electrons</u>

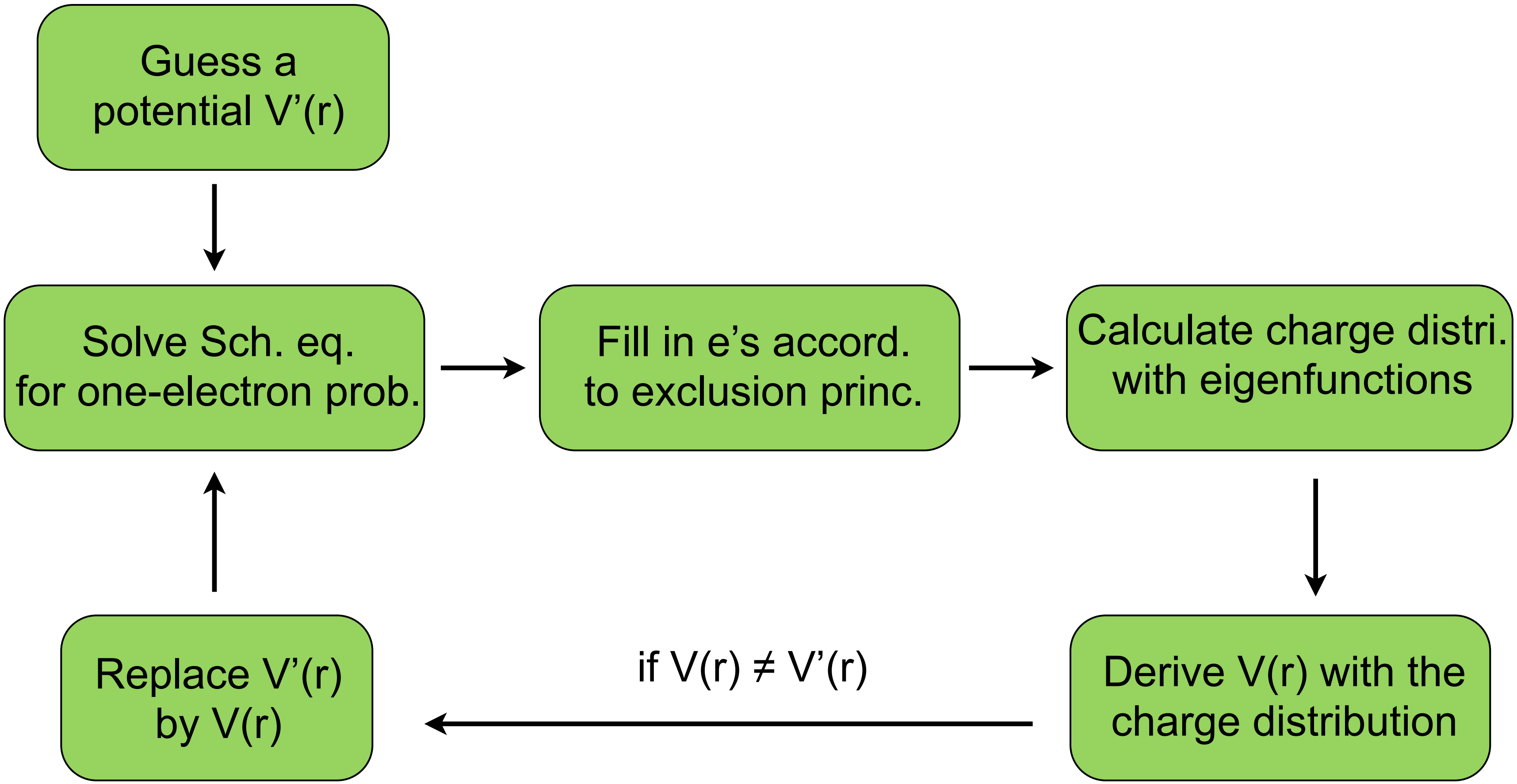
$$\left[\sum_{i=1}^{Z}\left(\frac{\mathbf{p}_i^2}{2m_e}-\frac{Ze^2}{4\pi\varepsilon_0 r_i}\right)+\sum_{i>j}\sum_{j}\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_i-\mathbf{r}_j|}\right]\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_Z)$$
$$=E\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_Z)$$

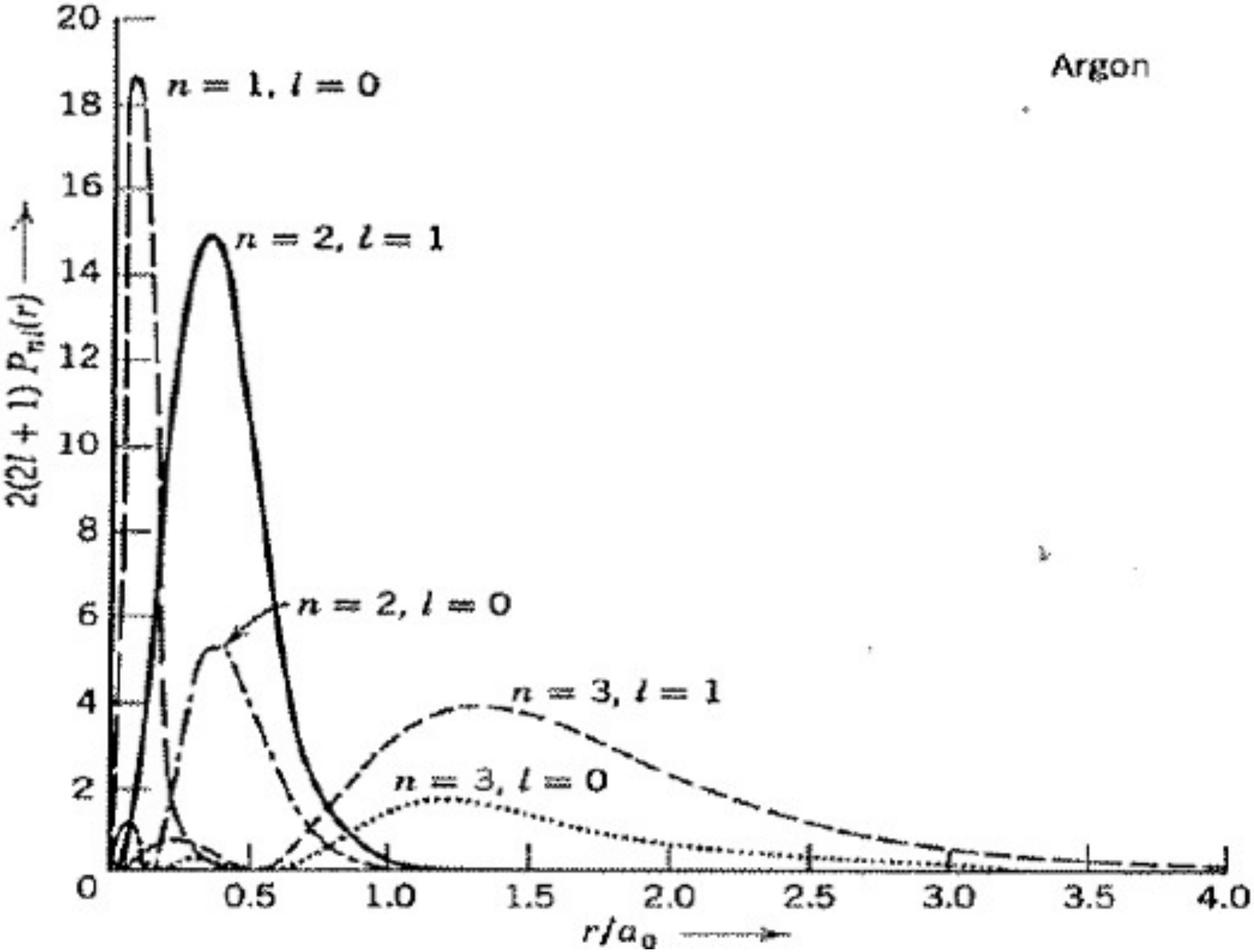
V(r)

The method makes the following major simplifications in order to deal with this task:

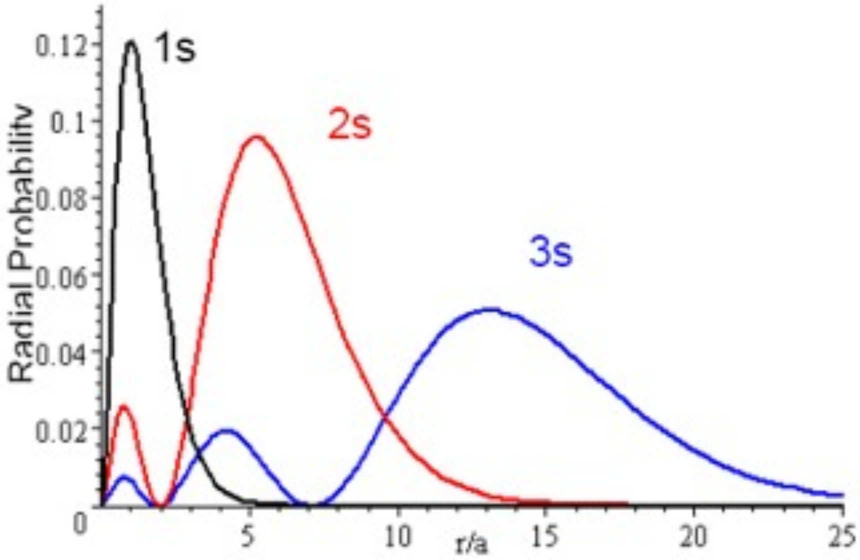
- The Born–Oppenheimer approximation is inherently assumed. The full molecular wave function is actually a function of the coordinates of each of the nuclei, in addition to those of the electrons.
- Typically, relativistic effects are completely neglected. The momentum operator is assumed to be completely non-relativistic.
- The variational solution is assumed to be a linear combination of a finite number of basis functions, which are usually (but not always) chosen to be orthogonal. The finite basis set is assumed to be approximately complete.
- The mean field approximation is implied. Electrons are moving independently in a spherically symmetrical net potential.

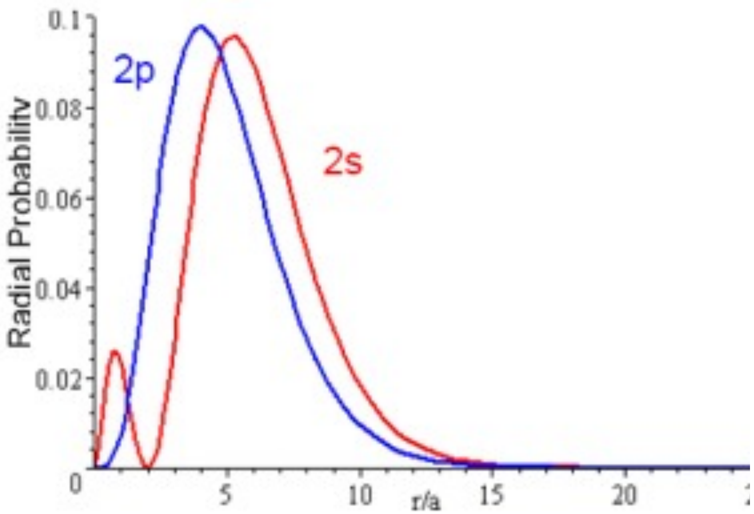
Algorithm for Hartree Approximation

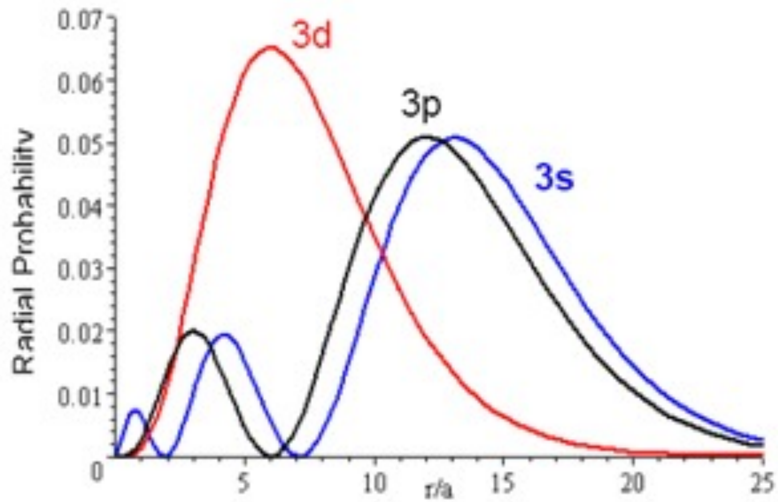


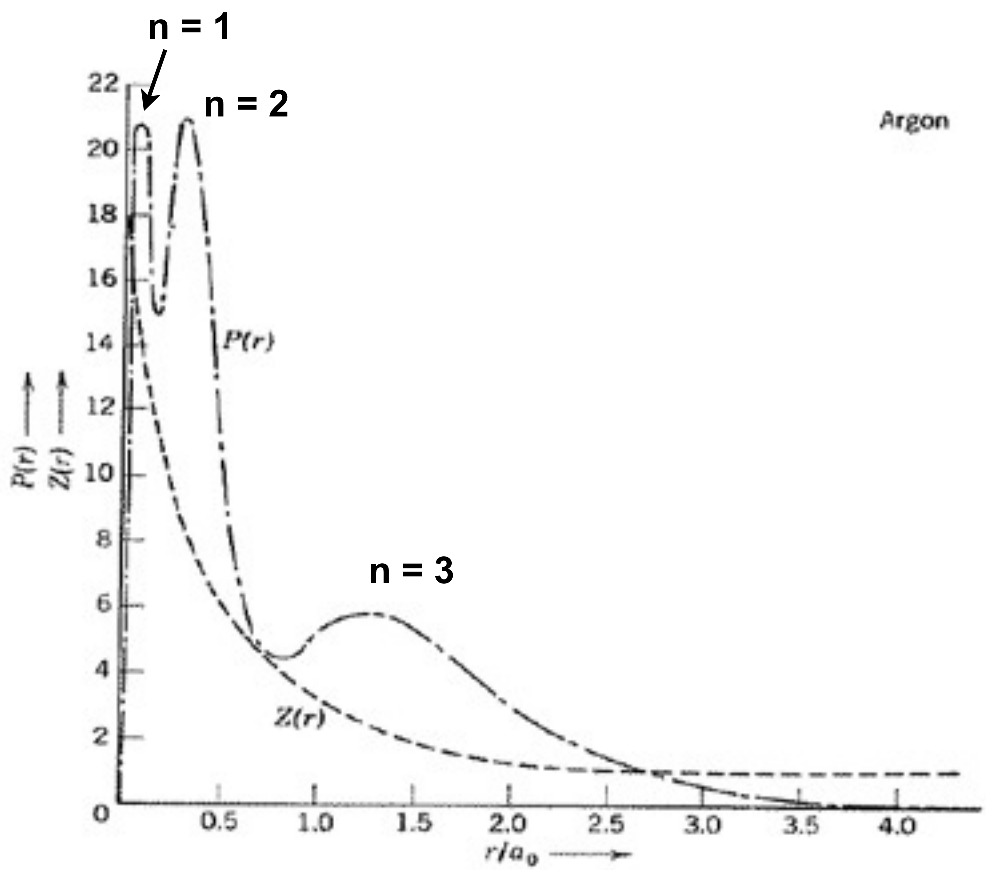


Argon
$n = 1, l = 0$
$n = 2, l = 1$
$n = 2, l = 0$
$n = 3, l = 1$
$n = 3, l = 0$
$2(2l + 1)\, P_{nl}(r)$
r/a_0
0
2
4
6
8
10
12
14
16
18
20
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0


Radial Probability
r/a
1s
2s
3s
0
0.02
0.04
0.06
0.08
0.1
0.12
5
10
15
20
25


Radial Probability
r/a
2p
2s
0
0.02
0.04
0.06
0.08
0.1
5
10
15
20

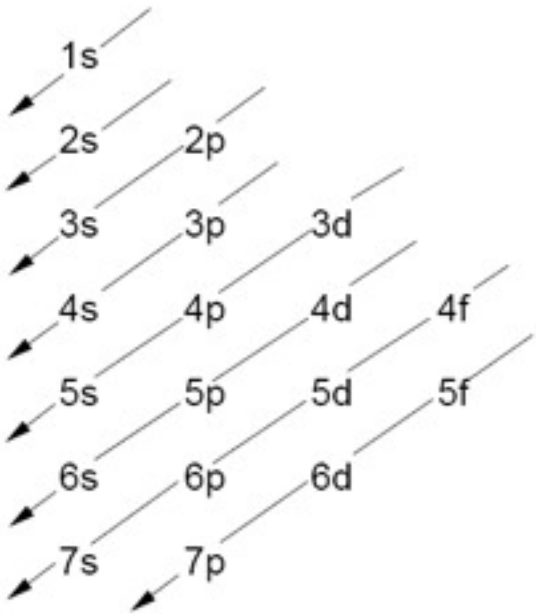

Radial Probability
r/a
3d
3p
3s
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
5
10
15
20
25

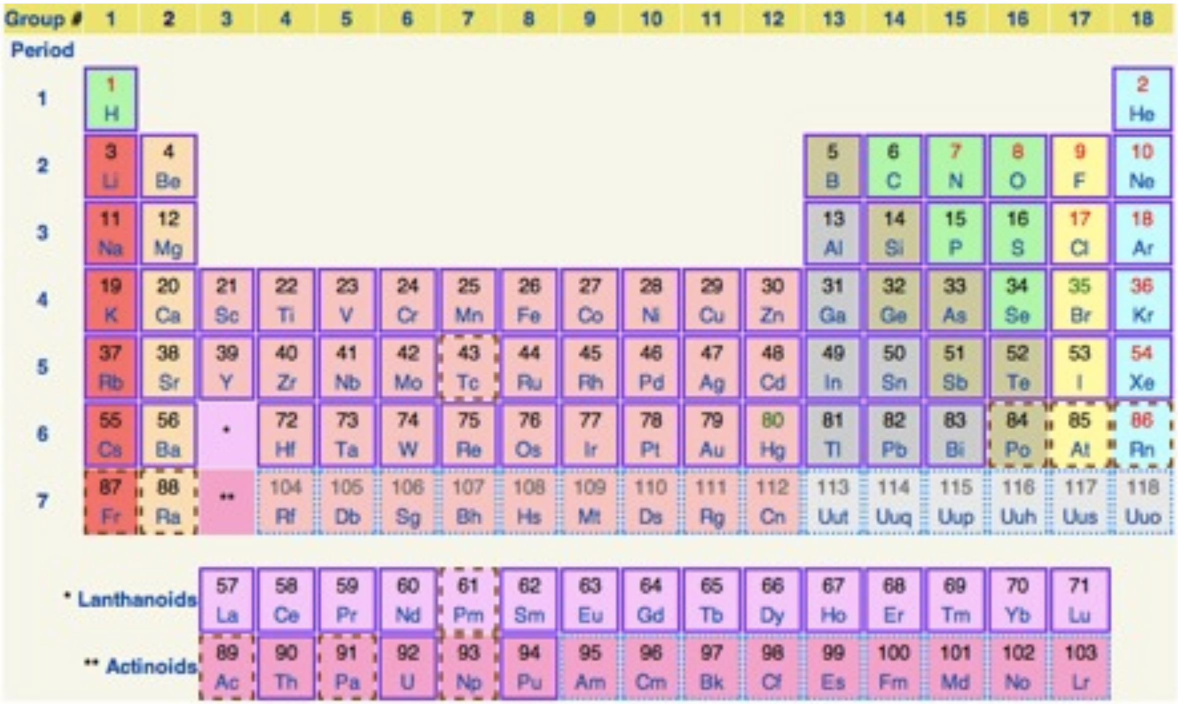


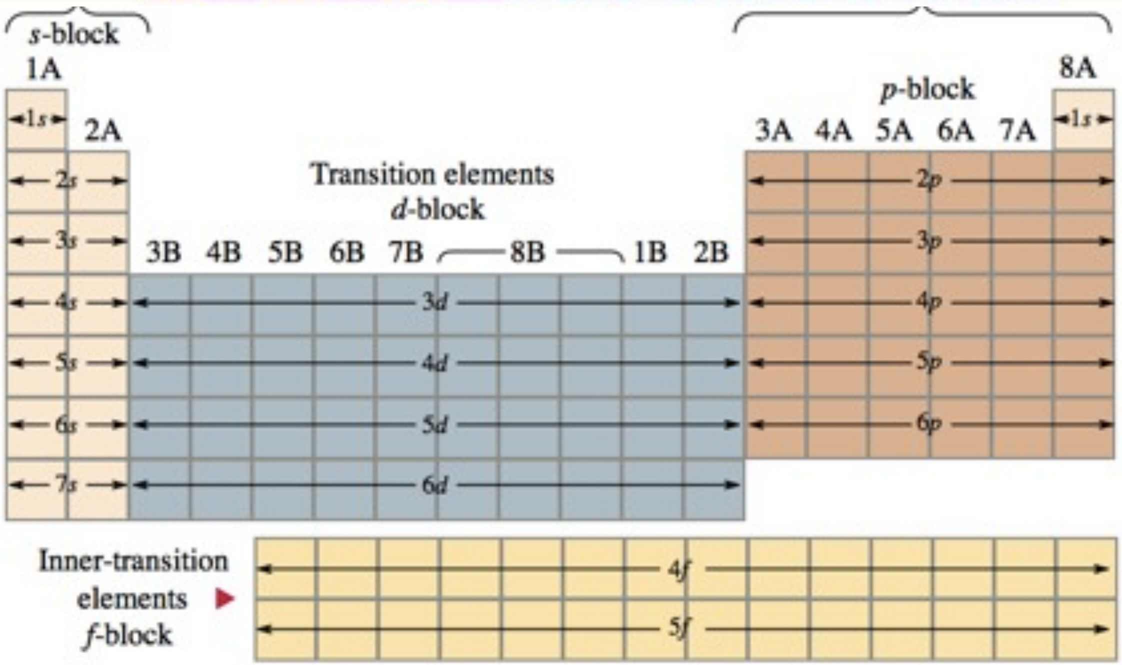
$$V(\mathbf{r}) = -\frac{Z(r)}{4\pi\epsilon_0}\frac{e^2}{r}$$

$$Z(r) = \begin{cases} Z, & r \to 0 \\ 1, & r \to \infty \end{cases}$$

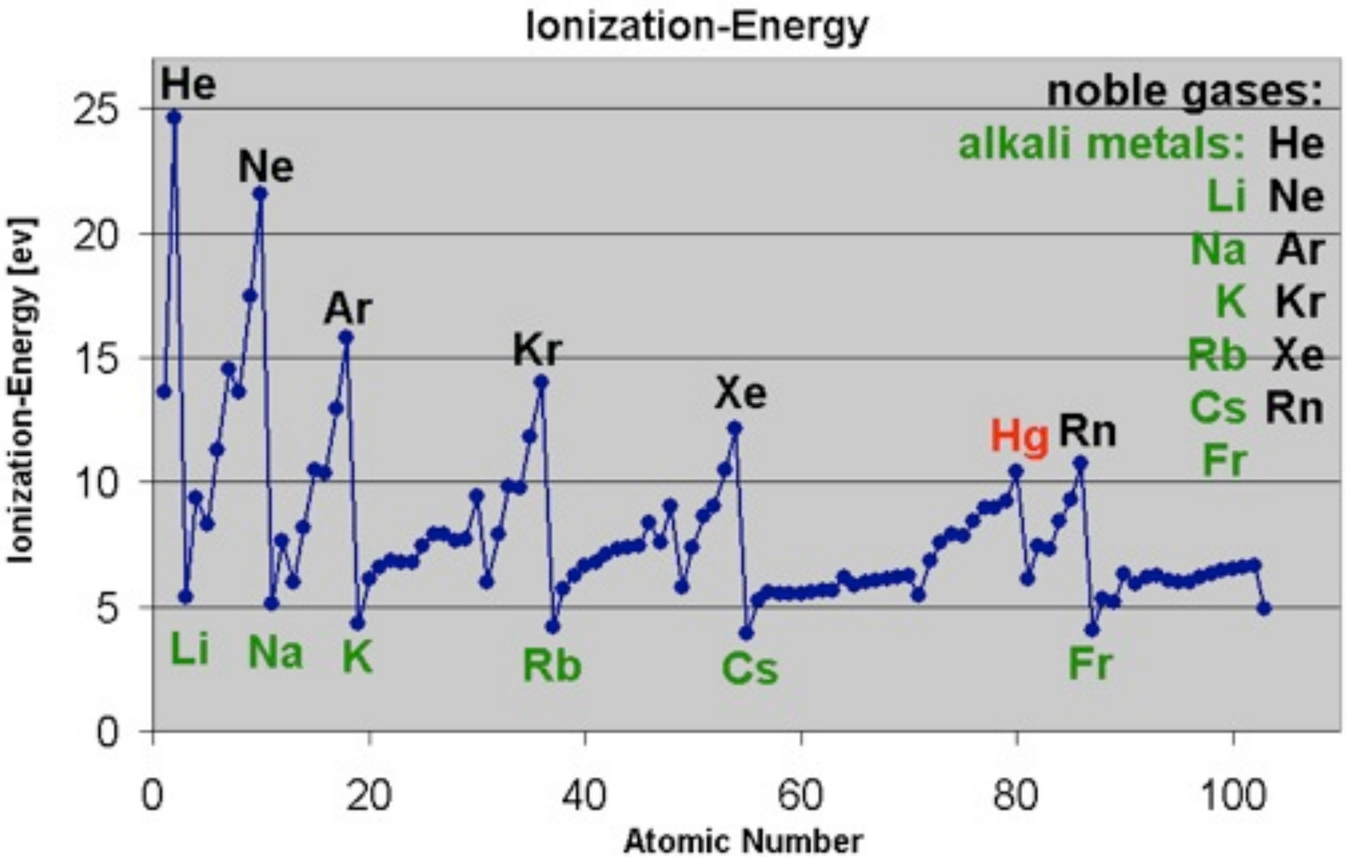
Aufbau principle




Group # 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Period
1 1 H 2 He
2 3 Li 4 Be 5 B 6 C 7 N 8 O 9 F 10 Ne
3 11 Na 12 Mg 13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
4 19 K 20 Ca 21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn 31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
5 37 Rb 38 Sr 39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd 49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
6 55 Cs 56 Ba * 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn
7 87 Fr 88 Ra ** 104 Rf 105 Db 106 Sg 107 Bh 108 Hs 109 Mt 110 Ds 111 Rg 112 Cn 113 Uut 114 Uuq 115 Uup 116 Uuh 117 Uus 118 Uuo
* Lanthanoids 57 La 58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu
** Actinoids 89 Ac 90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr


s-block
1A
1s
2A
2s
3s
4s
5s
6s
7s
Transition elements
d-block
3B 4B 5B 6B 7B 8B 1B 2B
3d
4d
5d
6d
p-block
8A
3A 4A 5A 6A 7A
1s
2p
3p
4p
5p
6p
Inner-transition
elements
f-block
4f
5f

First Ionization Energy



Homework#7 (Oct. 25, 2010):

For the argon atom, the values of Z_n are determined with Z_1 = 16, Z_2 = 8, and Z_3 = 3. Use these values to estimate the radii of the n = 1, 2, and 3 shells of the atom.